

Methane: Interhemispheric concentration gradient and atmospheric residence time

(atmospheric OH/trace composition/interhemispheric transport/Amazon basin)

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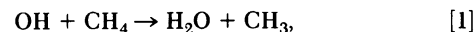
ABSTRACT The ground level concentrations of methane in the atmosphere have been measured to be in the range from 1.45 to 1.62 parts per million by volume (ppmv) of dry air in remote locations between 62°N and 54°S latitudes during the time period from November 1977 to July 1979. The average (\pm rms) concentration for the northern hemisphere was 1.57 ± 0.02 ppmv in January 1978 and 1.59 ± 0.02 in July 1979. The average concentration in the southern hemisphere was lower— 1.47 ± 0.02 in January 1978 and 1.51 ± 0.01 in July 1979. The ratio of concentrations between the two hemispheres was 1.068 ± 0.016 in January 1978 and 1.055 ± 0.013 in July 1979, for an average of 1.06 ± 0.01 . The higher concentrations in the northern hemisphere require either that the sources of methane lie preferentially in the northern hemisphere or that the removal processes operate more rapidly in the southern hemisphere or both. The primary removal process for CH_4 is reaction with tropospheric OH radicals and its estimated atmospheric lifetime is 10.5 ± 1.8 yr. The observed interhemispheric gradient is consistent with this lifetime and preferential release of methane in the northern hemisphere. Measurements taken in the Amazon basin region indicate the presence of a substantial source of methane in that area.

The major hydrocarbon present in the natural atmosphere of the earth is methane, which is found in a relative concentration of ≈ 1.6 parts per million by volume (ppmv) throughout the troposphere (1–3). Most hydrogen and most carbon in the atmosphere are found in oxidized forms, and CH_4 is subject to relatively rapid oxidation to other chemical forms. The major sources for the continuous replenishment of atmospheric CH_4 certainly involve gaseous evolution from biological material under anaerobic conditions—e.g., rice paddies, swamps, enteric fermentation, etc.—but are not known in any precise quantitative detail. The overall biological origin of most of the atmospheric CH_4 is inferred from the near-equivalence between the $^{14}\text{C}/^{12}\text{C}$ ratio in it to that in living material that draws both $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$ from the atmosphere (1–4). Any carbonaceous material isolated for $>20,000$ yr from exchange with the cosmic ray-produced atmospheric ^{14}C reservoir will have a negligible ^{14}C content. Hence, the contribution to atmospheric CH_4 from the flaring of natural gas, or by volcanoes, earthquakes, etc. (5), cannot be major because these sources should be essentially devoid of ^{14}C . Ehhalt (3) has placed an upper limit of 10% on the nonbiogenic sources of CH_4 .

Methane has been known as a component of the atmosphere since 1948 (6), and several groups have reported (Table 1) higher concentrations in the northern than in the southern hemispheres (7–15, ¶). A consensus developed in the late 1970s that a concentration gradient does indeed exist between the two hemispheres. Ehhalt (10) has further demonstrated that the

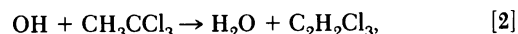
presence of N/S hemispheric gradients in methane concentrations provides some boundary conditions on the atmospheric residence time of CH_4 and upon the N/S distribution of its sources and sinks.

During 1977–1979 we carried out three series of measurements of CH_4 concentrations in tropospheric samples collected in remote locations at the surface between 62°N and 54°S latitudes, and we have consistently observed a N/S gradient with ≈ 5 –7% higher concentrations in the north than in the south. The removal of CH_4 from the atmosphere is usually assumed to occur almost entirely by reaction 1 with OH radicals,



with most of this attack occurring in the lowest 6 km of the atmosphere. Quantitative estimates of the overall rate of this reaction are limited by the current imprecision in the knowledge of worldwide concentrations of OH in both time and space. In the absence of better information concerning sources and sinks, the atmospheric residence time of CH_4 has not yet been well established and further data can be very useful. Previous estimates of the atmospheric residence time for CH_4 have ranged from 1.5 (16) or 2 (17) yr to much longer times of 21.5 (12) or 29 (18) yr. Ehhalt (10) has recently estimated a most probable value of about 5 yr with a range from 2.5 to 11 yr.

The variations in CH_4 concentrations in our samples correlate well with the variations in CH_3CCl_3 concentrations measured in the same canisters, for which a considerably larger N/S gradient was observed (19). Because the major removal process for CH_3CCl_3 also involves reaction with OH radicals in the troposphere, as in Eq. 2,



measurement and evaluation of CH_4 and CH_3CCl_3 concentrations from the same air parcels can provide still further information about the sources for CH_4 and the geographical location of the sinks for both compounds. The CH_3CCl_3 is released to the atmosphere anthropogenically, with about 95% going first into the northern hemisphere, most of it in the temperate zone. The annual release rates for CH_3CCl_3 have risen sharply during the past decade.

The observation of a N/S hemispheric gradient in the con-

Abbreviations: ppmv, concentration in parts per 10^6 by volume; ITCZ, Intertropical Convergence Zone, meteorologically separating northern and southern hemispheres; N/S, north/south; NBS, National Bureau of Standards.

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Table 1. Measurements of N/S interhemispheric gradients in CH₄ concentrations

Time period	Ref.	N/S ratio	Northern		Southern	
			Concentration	Latitude	Concentration	Latitude
Mar.–Apr. 1975	7	Infrared spectroscopy, concentrations in atm-cm				
		1.2	1.46–1.58	13°N–57°N	1.22–1.40	23°S–67°S
		Instrumental gas analysis, concentrations in ppmv				
Nov.–Dec. 1972	8, 9	1.06	1.44 ± 0.04	7°N–33°N	1.36 ± 0.04	5°N–75°S
Nov.–Dec. 1972	10	1.08	1.40 ± 0.02	0°–30°N	1.30 ± 0.01	5°N–75°S
Nov.–Dec. 1972	11*	1.08	1.68		1.56	
Sep.–Dec. 1977	12, 13	1.03	1.43 ± 0.07	0°–65°N	1.39 ± 0.05	0°–90°S
Jan. 1978	†	1.07	1.58	10°N–56°N	1.47	20°S–54°S
Apr.–May 1978	14	1.06	1.72	N of 20°N	1.62	S of ITCZ
May 1979	15	1.06	1.595	45°N	1.510	43°S
Jan. 1978	This work	1.068 ± 0.016	1.565 ± 0.017	10°N–56°N	1.466 ± 0.015	20°S–54°S
July 1979	This work	1.055 ± 0.013	1.593 ± 0.020	10°N–62°N	1.509 ± 0.005	8°S–54°S

N/S, north/south; ITCZ, Intertropical Convergence Zone.

* Data of ref. 10 corrected upward by 1.2 from calibration change.

† Footnote †.

centration of a trace gas requires either (i) the source of the gas be predominantly in one hemisphere or (ii) the removal rate be more rapid in one hemisphere than the other. The former is certainly the case for many anthropogenic gases that are released largely in the northern hemisphere, including CO₂ from fossil fuel combustion (20), ⁸⁵Kr from nuclear fission (21), and CCl₃F, CCl₂F₂, and other industrially significant chlorine-containing molecules (22). There have also been suggestions that the average tropospheric OH concentration might be higher in the southern hemisphere than in the northern (23-27), such that removal of CH₄ and CH₃CCl₃ by reaction with OH would therefore occur more rapidly in the south than in the north. Because most of the known biological sources of CH₄ are essentially land-based, the primary release of atmospheric CH₄ into the northern hemisphere has been strongly indicated (10). Although biological in character and of long-standing historically, the release of CH₄ from cultivated rice fields and from much of the enteric fermentation can also be assigned as essentially of anthropogenic origin. Both the world land area devoted to the cultivation of rice and the number of domesticated large mammals have increased during the past two decades (28, 29).

EXPERIMENTAL PROCEDURES

We have collected ground-level air samples from rural locations (identified by nearby communities in Tables 2 and 3) between 62°N and 54°S latitudes, usually within a period of several weeks for N/S comparisons. The samples were collected in 2-liter stainless steel canisters each equipped with a single Nupro stainless steel valve. The canisters were evacuated in the laboratory, transported to and opened in the remote environments, and then returned to the laboratory for analysis by gas chromatography. Aliquots were first measured for CH₃CCl₃ concentrations by electron-capture gas chromatography. Further aliquots were then used for CH₄ analysis with flame ionization as the detection technique, and finally, still others were used for CCl₃F and CCl₂F₂ measurements by electron capture detection.

Two different procedures were used in the analysis of the November 1977 to February 1978 samples. In the first procedure, † aliquots were taken directly from the stainless steel sample canisters at room temperature and were analyzed by using helium as the carrier gas in the flame-ionization gas chromatography. The CH₄ concentrations so measured were then corrected to ppmv in dry air from the absolute humidities measured at the time of collection. These absolute humidities varied from 3 torr (1 torr = 1.333 × 10² pascal) (Idaho) to 21 torr (St. Croix), a variation of almost 3% in the contribution of H₂O to

the total measured pressure. These data were reported by Mayer *et al.* †. The second procedure, used for all of the data reported here, involves freezing out less volatile components (including H₂O) at -20°C, with N₂ as the carrier gas for a more stable baseline and greater sensitivity in the flame-ionization measurements. The CH₄ concentrations listed in the tables are the average of alternate data taken usually from five aliquots of the sample and five aliquots from a secondary standard.

The CH₄ concentrations for these samples are summarized in Tables 2 and 3, expressed as ppmv of dry air, and are grouped generally by the dates of collection. The precision of the measurements of the CH₄ content of each individual sample canister is estimated to be <±0.01 ppmv. All of the sample measurements in each of the groups of Table 2 and those of Table 3 were made in the laboratory during time periods of about 1 month to permit more accurate between-sample comparisons, and are estimated to have a precision within each group of ±0.01 relative to one another. Repetitive measurements of the same set of samples 1-3 months later showed no changes in either the absolute or relative values beyond normal statistical variability, indicating that the air samples preserve the integrity of the CH₄ concentrations over long periods of storage. The Ivanpah sam-

Table 2. Ground-level tropospheric concentrations during 1977-1978

Latitude	Sampling location	Date	ppmv
55.5°N	Ketchikan, AK	1/21/78	1.580
43.4°N	Twin Buttes, ID	11/ 1/77	1.574
35.3°N	Ivanpah, CA	11/ 8/77	1.560
25.2°N	Key Largo, FL	2/ 1/78	1.584
17.8°N	St. Croix, VI	2/ 3/78	1.555
13.7°N	St. Lucia, B.W.I.	2/ 5/78	1.539
16.2°S	Rio Zongo, Bolivia	1/14/78	1.565
23.5°S	Antofagasta, Chile	1/12/78	1.458
36.8°S	Concepcion, Chile	1/ 6/78	1.496
41.5°S	Puerto Montt, Chile	1/ 8/78	1.453
45.7°S	Coihaique, Chile	1/10/78	1.461
45.8°S	Balmaceda, Chile	1/ 9/78	1.462
53.5°S	Punta Arenas, Chile	1/ 8/78	1.467
31.7°N	Punta Banda, Mexico	8/ 9/78	1.556
31.6°N	Santo Tomas, Mexico	8/ 9/78	1.613
21.3°S	Rarotonga, Cook Is.	9/21/78	1.498
21.3°S	Rarotonga, Cook Is.	9/22/78	1.482
21.3°S	Rarotonga, Cook Is.	9/23/78	1.498
42.7°S	Hokitika, N.Z.	8/30/78	1.494
43.8°S	Knights Point, N.Z.	8/31/78	1.494
45.5°S	Manipouri, N.Z.	9/ 2/78	1.478

Table 3. Ground-level tropospheric concentrations during 1979

Latitude	Sampling location	Date	ppmv
61.8°N	Chickaloon, AK	6/18/79	1.617
61.7°N	Willow, AK	6/18/79	1.609
55.5°N	Ketchikan, AK	6/19/79	1.619
55.5°N	Ketchikan, AK	6/19/79	1.608
47.2°N	Copalis Beach, WA	6/20/79	1.609
44.2°N	Roosevelt Beach, OR	6/20/79	1.592
40.4°N	Cape Mendocino, CA	6/21/79	1.607
25.0°N	Islamorada, FL	7/14/79	1.569
22.8°N	Long Island, Bahamas	7/15/79	1.568
20.0°N	Lanpahoehe, HI	4/ 7/79	1.566
17.8°N	St. Croix, VI	7/17/79	1.581
13.3°N	North Point, Barbados	7/18/79	1.571
10.5°N	Biche, Trinidad	7/21/79	1.587
10.3°N	Mayaro, Trinidad	7/21/79	1.570
5.4°N	Powakka, Surinam	7/20/79	1.555
1.2°S	Belem, Brazil	6/ 9/79	1.574
3.1°S	Manaus, Brazil	6/10/79	1.601
3.1°S	Manaus, Brazil	6/10/79	1.577
3.6°S	Fortaleza, Brazil	6/ 8/79	1.546
8.1°S	Recife, Brazil	6/ 7/79	1.512
13.0°S	Salvador, Brazil	6/ 7/79	1.509
19.2°S	Vitoria, Brazil	6/ 5/79	1.511
23.5°S	Antofagasta, Chile	6/ 2/79	1.504
41.4°S	Puerto Montt, Chile	5/29/79	1.503
53.1°S	Punta Arenas, Chile	5/31/79	1.517

ple from November 1977 has been remeasured several times over the 4-yr period since collection without change in its indicated concentration of CH_4 . The agreement in measured concentrations of CH_4 for samples treated by both procedures was excellent, with somewhat better precision for the N_2 -carrier freeze-out method, and the latter has been adopted as the standard method of analysis of subsequent samples. The current procedure utilizes a 91.5-cm, 80/100-mesh Spherocarb chromatographic column packed in 3.18-mm stainless steel and operated at 75°C. The CH_3CCl_3 concentrations in the same canisters are not as readily preserved as CH_4 but have generally also remained stable over periods of 2 or more months.

The concentrations in ppmv for the individual samples of Table 3 are graphed in Fig. 1 versus the concentration of CH_3CCl_3 in parts per 10^{12} by volume found in the same canister (unpublished data). Because the dominant tropospheric removal process for each is reaction with OH, as in Eqs. 1 and 2, the concentrations for these two molecules can be anticipated to have some correlation with one another. However, much of the CH_4 is introduced into the atmosphere in tropical regions, whereas most of the CH_3CCl_3 is released in the north temperate zone, and this difference in source location could readily reduce any correlation induced by the similarity in location of the sinks. The period of time around June–July 1979 offered a favorable opportunity for observation of a $\text{CH}_4/\text{CH}_3\text{CCl}_3$ correlation because both the northern (10°N–62°N) and southern (0°–54°S) hemispheres were well mixed at that time, as indicated by CCl_3F and CCl_2F_2 concentrations, with a sharp gradient between 0° and 10°N at the ITCZ.

An excellent linear correlation ($R^2 = 0.97$) is observed for the CH_4 and CH_3CCl_3 concentrations from 20 of the canisters, as indicated in Fig. 1. The five remaining points all deviate in the direction of having "excess" CH_4 and are all located within the Amazon River basin of northern South America. The three northernmost Brazilian locations all clearly contained "southern hemispheric" concentrations of CCl_3F and CCl_2F_2 , whereas that from Surinam had concentrations of these chlorofluorocarbons intermediate between the northern and southern values (unpublished data). We attribute the additional CH_4 in

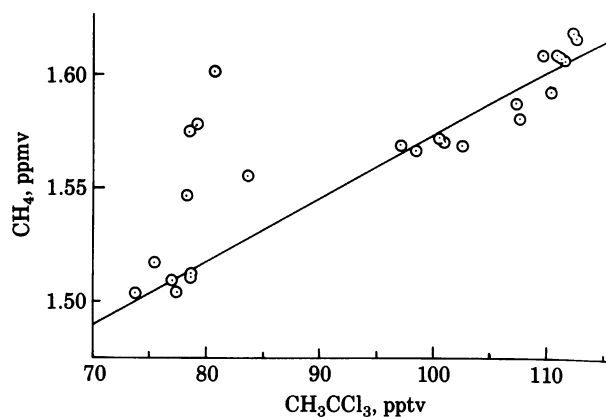


FIG. 1. Correlation of measured concentrations of CH_4 and CH_3CCl_3 in tropospheric samples in mid-1979. pptv, concentration in parts per 10^{12} by volume.

these five samples to the presence of a substantial Amazon basin source of CH_4 from the anaerobic decay of biological material. Approximate estimates from these very limited data suggest that the Amazon basin could be the source for as much as 10% of the atmospheric methane.

We calculate an average southern hemispheric CH_4 concentration of 1.466 ± 0.015 in January 1978 and 1.491 ± 0.009 in August–September 1978. We omit the Amazon basin measurements in Table 3 and calculate a southern hemispheric concentration of 1.509 ± 0.005 for July 1979 over the latitude range from 8°S to 54°S. The difference in CH_4 concentrations between January 1978 and July 1979 appears to be significant (30). Our northern hemispheric average for January 1978 is 1.565 ± 0.017 and for July 1979 is 1.593 ± 0.020 . The corresponding ratios of N/S concentrations are 1.068 ± 0.016 in January 1978 and 1.055 ± 0.013 in July 1979 for an average value of 1.06 ± 0.01 . Our average value for the interhemispheric gradient is in good agreement with other recent measurements insofar as the ratio of concentrations is concerned.

ABSOLUTE CONCENTRATIONS

Our absolute concentrations were determined by direct comparison with secondary standards prepared from a primary standard furnished by Matheson and stated to have an absolute concentration of 48.9 ppmv with an absolute accuracy of $\pm 1\%$, as determined by comparison with a National Bureau of Standards (NBS) standard. Cross-comparison showed the absolute concentration in one such secondary standard as 1.499 ppmv on the basis of vacuum-line dilution from the Matheson standard and 1.499 on the basis of direct comparison with a 0.97 ppmv NBS standard. The close agreement suggests that laboratory preparation of secondary standards can be done with a precision equal to or better than the accuracy of the absolute concentration measurements. The response of the flame ionization detector is linear with concentration over the range between two separate NBS standards at 0.97 and 4 ppmv within the accuracy of the measurements ($\pm 0.5\%$) and should certainly be linear over the observed 1.45- to 1.62-ppmv range of CH_4 concentrations found in these samples of background tropospheric air.

Our data in Tables 2 and 3 are given in ppmv of dry air, whereas some of the other measurements of Table 1 appear to be expressed in terms of air with natural humidity, judging from the experimental descriptions. Because some of these measurements are made at surface level in the tropics and others are from aircraft flying at altitudes with ambient temperatures below 0°C, the natural humidity undoubtedly varies widely. In our own data, the 21-torr water vapor concentration in the St. Croix sample corresponds to a dry air concentration of CH_4

0.044 ppmv higher than the moist air concentration of CH₄ quoted for the same air.

The historical record of recent measurements of absolute CH₄ concentrations is not very consistent, as evidenced in Table 1, so it is difficult to establish whether small variations in observed methane concentration have occurred during the period 1972–1979 (30). Agreement upon values of about 1.4 ppmv in the north and 1.3 ppmv in the south apparently existed earlier among the separate data from the same 1972 voyage (8–10). This concordance has been removed by the discovery of an error of a factor of about 1.2 in a calibration standard used in the National Center for Atmospheric Research measurements before 1974 (11). When this correction factor is included, one set of these 1972 measurements then lies above our present values and one lies below it. We are unable to explain the discrepancy among these 1972 values and therefore unable to draw any conclusions about possible longer term trends in CH₄ concentrations except those occurring internally within our own data set. It seems probable from the spectroscopic records back to 1948 (6) that no large variation ($\geq 20\%$) has occurred over the past 30 yr.

ATMOSPHERIC LIFETIME OF CH₄

If reactions 1 and 2 are the predominant mechanisms for atmospheric removal of CH₄ and CH₃CCl₃, respectively, then the removal rates are proportional to the reaction rate constants, k_1 and k_2 , at each location in the atmosphere, and the relatively uncertain OH concentrations in the atmosphere can be essentially canceled out in a relative calculation. The best current rate constant equations for these reactions are (31) $k_1 = 2.4 \times 10^{-12} \exp(-1710/T)$ and $k_2 = 5.4 \times 10^{-12} \exp(-1820/T)$ cm³mol⁻¹s⁻¹. Although the available temperature range in the troposphere covers about 90°C, $\approx 80\%$ of the removal of these molecules occurs below an altitude of 6 km, at temperatures above 275 K, with the median altitude for such reaction at about 2 km (32). At the higher altitudes the lower temperatures reduce the rate constants for reactions 1 and 2 so that they are 1/8th as fast at 217 K as at 288 K. The lower absolute concentrations of well-mixed gases (factor of 4 between altitudes of 0 and 12 km) further decrease the actual reaction rates until the removal rate at 12 km for a given OH concentration is about 1/30th of that for the same concentration at the surface. Because the activation energies for reactions 1 and 2 are very similar, the ratio k_2/k_1 varies only from 1.51 to 1.56 between 275–300 K, and the value at 280 K, 1.52, is an appropriate average value for the whole tropospheric reaction competition. By using the atmospheric lifetime of 6.9 ± 1.2 yr calculated for CH₃CCl₃ from its measured atmospheric loading in 1978 (19), the estimated lifetime for CH₄ is 1.52 times longer, or 10.5 ± 1.8 yr. The CH₃CCl₃ lifetime estimate is based upon removal by all processes—not just reaction with tropospheric OH—but is certainly dominated by the latter.

The existence of a N/S gradient in concentrations of CH₄ also provides some limitations on its atmospheric lifetime, through examination of the location and magnitude of its sources and sinks (10). Considerable insight into these relationships can be gained through a two-box N/S model of the atmosphere, as shown by Ehhlalt (10). The observation of essentially only two atmospheric concentrations (one north of 10°N and one south of 0°) for CCl₃F and CCl₂F₂ in July 1979 (unpublished data) demonstrates that the two-box model approach has substantial validity in the real atmosphere for discussions of concentration gradients for trace gases.

Ehhlalt has developed a formula relating in steady state the average atmospheric lifetime, τ_a , through Eq. 3,

$$\tau_a = \tau_m \frac{M_s - M_n}{(\alpha + 1)(M_n - M_s)}, \quad [3]$$

to the average interhemispheric mixing time, τ_m , the concentrations in the north and south (M_n , M_s), and the ratio, α , of the source strengths in the northern and southern hemispheres (10). He then adopted τ_m as 1 yr and calculated τ_a from his 1972 data (Table 1) in which $M_n = 1.40$ ppmv and $M_s = 1.30$ ppmv for a difference of 0.10 ppmv. An equivalent formula to Eq. 3 is given in Eq. 4, in which the interhemispheric concentration ratio,

$$\tau_a = \tau_m \frac{(\alpha - R)}{(\alpha + 1)(R - 1)}. \quad [4]$$

$R = M_n/M_s$ has been used instead of the individual concentrations. Because most biogenic CH₄ is land-based, production must be predominantly in the northern hemisphere. Ehhlalt postulated that CH₄ production might be approximately proportional to the land area in each hemisphere ($\alpha = 2.06$) or more likely to that below 60° in each hemisphere ($\alpha = 2.4$), and he calculated the most probable lifetime for CH₄ to be 5 yr. Values of 2.5 and 11 yr were calculated for interhemispheric gradients of 0.15 and 0.05 ppmv, respectively, on the old calibration scale. The change in the National Center for Atmospheric Research absolute calibration (11) changes the absolute values of M_n and M_s but not those of R or τ_a .

The formulation of Eqs. 3 and 4 implicitly adopts the additional assumption that the rate of removal of CH₄ is the same in both the northern and southern hemispheres—i.e., that there is no hemispheric asymmetry in the average OH radical concentrations. Several atmospheric model calculations have been performed which lead to questioning of the hemispheric equivalence in OH concentrations (23–27, 32), with some hypothesizing asymmetries as large as a factor of 3. The observed CH₃CCl₃ gradient in concentrations has led to suggestions that the OH concentrations are twice as large in the southern as in the northern hemisphere (26). Other analyses place the ratio between 1.0 and 1.3 (27).

We have expanded the Ehhlalt two-box model to include the additional possibility of hemispheric asymmetry in the removal of CH₄ and CH₃CCl₃ by reaction with OH, and we have defined the interhemispheric mixing rate as k ($=\tau_m^{-1}$) and the two removal rates as λ_n and λ_s , with the ratio $\Lambda = \lambda_s/\lambda_n$. With different removal rates in the two hemispheres the average lifetime, τ_a , is no longer rigorously defined because the lifetime is now dependent upon the hemisphere in which the trace gas is released. However, with lifetimes of 5 yr or longer and interhemispheric mixing times of about 1 yr, the average atmospheric lifetimes are at most a few percent different for the same molecule introduced into the northern versus the southern hemispheres. We therefore define an average loss rate in steady state, λ_a , by Eq. 5,

$$\lambda_a = \frac{(\lambda_n R + \lambda_s)}{R + 1}, \quad [5]$$

and an average lifetime, $\tau_a = \lambda_a^{-1}$, and assume its approximate applicability to any source distribution of gases introduced into the model. The differential equations for variation in the concentrations (M_n , M_s) are then given by Eqs. 6 and 7,

$$\frac{d(M_n)}{dt} = P_n - k(M_n - M_s) - \lambda_n(M_n) \quad [6]$$

and

$$\frac{d(M_s)}{dt} = P_s + k(M_n - M_s) - \lambda_s(M_s), \quad [7]$$

in which P_n and P_s are the source functions into the northern and southern hemispheres, respectively, and $\alpha = P_n/P_s$. At steady state, both Eqs. 6 and 7 are equal to zero and R is given by Eq. 8.

$$R = \frac{\alpha(\lambda_s + k) + k}{(\lambda_n + k) + \alpha k} \quad [8]$$

Obviously, an interhemispheric gradient with $R > 1$ requires either $\alpha > 1$ or $\Lambda > 1$, and $\alpha > 1$ is already indicated from the distribution of land mass. The other important parameter in determining the magnitude of the gradient R is the relative size of k versus the removal rate λ_a —i.e., of τ_m versus τ_a . When the solutions to Eq. 8 are evaluated for the range of values generally appropriate to CH_4 (α , 1–3; Λ , 1–3; τ_m , 0.8–2 yr; τ_a , 5–10 yr), the results are found empirically to be fitted within a few percent by Eq. 9.

$$\frac{(\alpha/\Lambda)(\tau_m)}{(\tau_a)} = 6(R - 1). \quad [9]$$

The form of this equation indicates that possible percentage errors in all four parameters on the left-hand side are found to be approximately equal in importance. Although Eq. 9 could in principle be used to estimate τ_a for CH_4 , it is readily apparent that the combined errors in α , Λ , τ_m , and R are unlikely to be as small as the 17% error calculated for τ_a from comparison with the CH_3CCl_3 lifetime. However, consideration of the gradient in concentration can still be quite valuable in assessing whether the estimate of 10.5 ± 1.8 yr for τ_a is consistent with the gradient and in furnishing insight into the hemispheric asymmetry or lack of it for sources and sinks.

Our best value for τ_m is 1.25 ± 0.15 yr ($k = 0.8 \pm 0.1 \text{ yr}^{-1}$), obtained from consideration of the observed N/S gradients for CCl_3F and CCl_2F_2 (unpublished data). With values of R from 1.05 to 1.07, the value of τ_a becomes $[(\alpha/\Lambda)(1.25)/(6)(0.06 \pm 0.01)]$ or $(3.0\text{--}4.2)(\alpha/\Lambda)$ yr. With Ehhalt's (10) values of $\alpha = 2.4$ and $\Lambda = 1.0$, the lifetime range becomes 7.2–10 yr. Alternatively stated, an atmospheric lifetime of 10.5 yr and $R = 1.05\text{--}1.07$ requires that the product $(\alpha/\Lambda) = 2.5\text{--}3.5$, which is certainly within the expected range for the product of these two ratios. Much more information is needed on the geographical locations of either sources or sinks before the CH_4 gradient can be used to evaluate either (α) or (Λ) separately.

A global average concentration of 1.56 ppmv for CH_4 corresponds to about 4.2×10^{15} g in the atmosphere in steady state. With an average lifetime of 10.5 yr, the required global source strength for all CH_4 sources is then about 4.0×10^{14} g/yr. This source strength is somewhat less than the minimum values estimated for biogenic sources alone by Ehhalt of $5.7\text{--}8.3 \times 10^{14}$ g/yr (3). In his 1979 estimate (3), the individual biogenic source strengths were given in units of 10^{14} g/yr as: rice paddy fields, 2.8; swamps and marshes, 1.9–3.0; enteric fermentation, 1.0–2.0; freshwater lakes, 0.01–0.25; tundra, ≤ 0.03 ; and oceans, 0.01–0.17. He has also added 0.16–0.5 from coal mining and other industrial activity with an upper limit on non-biogenic sources of 10%. Recent measurements of CH_4 emission from California rice fields lead to an extrapolated value of 0.59×10^{14} g/yr for world emissions from rice fields (33). The experimental bases for all of these extrapolations to worldwide source totals are very thin, and the estimates for paddy fields and swamps could readily have been overestimated by an amount sufficient to bring the calculated source strength from the 10.5-yr lifetime into agreement with the summed minimum values from biogenic sources. Indeed, if the Cicerone–Shetter value of 0.59 is substituted for 2.8 in Ehhalt's estimates, the minimum biogenic release becomes 3.5×10^{14} g/yr, and the estimated source strength is then compatible with the lifetime of 10.5 yr (33). Though there is thus no necessary disagreement between yearly flux and lifetime, the ranges of possible values for the CH_4 sources are still very large. Direct observation of

the source strengths for CH_4 is certainly now of prime importance in establishing more quantitatively the details of the atmospheric methane cycle.

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